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The main objective of this research, performed by Ellen Kurt Hondrogiannis, a graduate student at the University of Tennessee, is to investigate the utility of the combination of spectroscopy and electrochemistry, or spectroelectrochemistry (SEC), for studies of redox processes in molten halides. The initial studies involved the use of UV-visible, Raman, and electron spin resonance SEC to identify the radical anion intermediate formed during the electrochemical reduction of tetrachloro-p-benzoquinone, or chloranil, in the basic (<50 mole percent AlCl_3) molten sodium chloroaluminate melt at 175°C (1). This anion intermediate had not been detected in this melt previously, since cyclic voltammetry shows only one wave which had previously been attributed to a single two electron reduction to the dianion (2).

UV-visible SEC was also used to study the electrochemical reduction of NbCl_5 in the basic AlCl_3 - $\text{NaCl}_{(\text{sat})}$ melt at 175°C (3). The SEC showed that $\text{Nb}_6\text{Cl}_{18}$ ($\text{Nb}^{2.33+}$) is electrochemically generated in the last reduction and that it can be oxidized through the $\text{Nb}^{2.50+}$ cluster to the $\text{Nb}^{2.67+}$ cluster. It was also shown that the $\text{Nb}^{2.33+}$ cluster is generated in each of the first three waves. This formation is believed to be due to the slow disproportionation of Nb^{4+} , formed during the first reduction wave, to Nb^{5+} and Nb^{3+} , the latter of which probably decomposes to form the subvalent cluster.

UV-visible SEC was also used to study the behavior of K_2ReCl_6 in the basic AlCl_3 - $\text{NaCl}_{(\text{sat})}$ melt at 175°C . The initial cyclic voltammograms obtained for K_2ReCl_6 solutions result in the formation of a new voltammetric wave at potentials more positive than the $[\text{ReCl}_6]^{2-}$ reduction. After this wave grows in, the equilibrium cyclic voltammogram for a solution of $[\text{ReCl}_6]^{2-}$ consisting of three reduction and two oxidation waves does not change. The new wave is believed to result from the $[\text{Re}_2\text{Cl}_9]^{2-}/[\text{Re}_2\text{Cl}_8]^{2-}$ couple; the second broad wave probably results from the reduction of both $[\text{ReCl}_6]^{2-}$ and $[\text{Re}_2\text{Cl}_8]^{2-}$. The very unstable $[\text{ReCl}_6]^{3-}$ yields $[\text{Re}_2\text{Cl}_8]^{2-}$, $[\text{ReCl}_6]^{2-}$, rhenium metal, and at least one other product. The presence of $[\text{Re}_3\text{Cl}_{12-x}]^{4-x}$ is believed to result from the slow decomposition of $[\text{Re}_2\text{Cl}_8]^{2-}$. The $[\text{Re}_3\text{Cl}_{12-x}]^{4-x}$ is stable in solution and is not reduced in the third reduction wave. The lack of decrease in the current in the third reduction even after 18 hours of electrolysis indicates that this step involves a catalytic regeneration of the starting material. X-ray powder diffraction of the particles produced in this step showed no evidence for rhenium metal. Further analyses of these particles using neutron activation, elemental analysis, inductively coupled plasma, and UV-visible reflectance and absorption spectroscopies did not aid in identifying this precipitate.

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